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(54) NON-AQUEOUS ELECTROLYTE FOR BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To prevent the deterioration of the structural material of a battery and the deterioration of battery performance even in the case where water intrudes the non-aqueous electrolyte by adding the organic silicon compound having Si-N coupling, which reacts with water and halogen acid so as to eliminate them, in the non-aqueous electrolyte including the support electrolyte, which reacts with water and generated the halogen acid.

SOLUTION: Organic silicon compound having Si-N coupling reacts with water and halogen acid, and the Si-N coupling is uncoupled for cleavage so as to decompose the water and halogen acid. Decomposition product after the reaction is harmless to the battery performance, and since the decomposition product is organic compound, it has affinity with the non-aqueous electrolyte. As an organic silicon compound having Si-N coupling, the organic silicon compound, which includes single or plural Si-N coupling in a molecule, is used, and the silicon compound, which has Si-N coupling in the shape of Si-N-Si coupling in a molecule, is used. Organosilazane compound and organo di-silazane compound are usually used.

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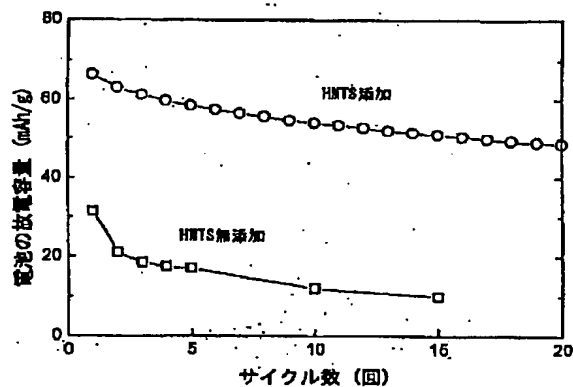
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(54) 【発明の名称】 電池用非水電解液

(57) 【要約】

【目的】 非水電解液電池において、水の混入に基づくハロゲン酸の発生を防止して、電池の劣化を防ぐ。

【構成】 水との反応によりハロゲン酸を生じ得る支持電解質を含む電池用非水電解液又はこれを用いた非水電解液電池において、水やハロゲン酸と反応してこれらを無害化する、Si-N結合を有する有機ケイ素化合物を添加する。



【特許請求の範囲】

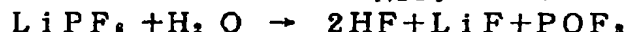
【請求項1】 水と反応してハロゲン酸を生じ得る支持電解質を含む非水電解液に、前記水及びハロゲン酸と反応してこれらを除去する、Si-N結合を有する有機ケイ素化合物を添加したことを特徴とする電池用非水電解液。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、電池用非水電解液に関し、更に詳しくは、例えば一定のハロゲン化合物等を支持電解質とした非水電解液を用いるリチウム二次電池等において、不可避免的に介在し得る少量の水分に起因してハロゲン酸が発生することへの対策を講じた電池用非水電解液に関する。

【0002】



【0005】フッ化水素は電池構成材料を劣化させ、更に電池性能を劣化させると言う問題がある。更に、前記「化1」の反応は高温域で促進されることが知られている。このため、例えば、 $-30^\circ\text{C} \sim 60^\circ\text{C}$ の温度域での安定的動作が要求される電気自動車のバッテリー用二次電池においては特に問題が顕著となり、 LiPF_6 を支持電解質とする非水電解液電池は適用が困難であるとされている。

【0006】そしてこの問題を解決するため、従来、次のような提案がされている。例えば特開平4-284372号公報に記載された非水電解液二次電池の発明においては、 LiPF_6 を支持電解質とする非水電解液に対し、 Al_2O_3 、 MgO 、 BaO から選ばれる酸化物を添加することにより、これらの酸化物が電解液に生じたフッ化水素を吸着し、反応系外へ除去する、としている。

【0007】又、特開平7-122297号公報に記載された非水電解液電池の発明においては、 LiPF_6 を支持電解質とする非水電解液に対し、酸無水物（例えば、無水酢酸）を添加することにより、これらの酸無水物が電解液中の水を予め捕捉して、前記「化1」の反応を抑制する、としている。

【0008】

【発明が解決しようとする課題】しかし、前記特開平4-284372号公報に記載の発明については、本件発明者の追試によれば、電池として現実的に許容し得る添加量の酸化物によっては、フッ化水素の除去は極めてゆっくりと進行するため、フッ化水素の発生速度に追いつかない。従って、フッ化水素による電池の劣化等を有効に防止するに至らない、と言う問題がある。

【0009】一方、前記特開平7-122297号公報に記載の発明については、酸無水物による脱水効果は高いが、その結果、酸無水物に起因する酸が発生することになり、いわば、ハロゲン酸を他の酸に置換するだけのことである。そしてハロゲン酸に対して例えば酢酸等は

*【従来の技術】リチウム又はその化合物を電極活物質に用い、そのことから電解液として支持電解質を含む有機溶媒を利用する非水電解液電池が、例えば電子部品用小型電源としての一次電池や、電気自動車のバッテリー用等に向けられる二次電池あるいはリチウムイオン電池等としてその有用性を注目されている。

【0003】これらの非水電解液電池において、上記の支持電解質には、例えばハロゲン化合物である LiPF_6 等が良く用いられているが、非水である筈の電解液中に若干の水分が不可避免的に混入していたり、あるいは他の電池材料からの吸着により生じた水分が存在していたりすると、次の「化1」に示すような反応が起こり、フッ化水素 HF のごときハロゲン酸が発生させる。

【0004】

【化1】

相対的に弱酸であるとは言え、やはり電解液や電池缶材料の劣化をもたらすことに変わりはなく、本質的な解決になっていない。

【0010】そこで本発明では、水と反応してハロゲン酸を生じ得る支持電解質を含む電池用の非水電解液、又はこれを用いた非水電解液電池において、ハロゲン酸による弊害を有効に防止し、しかも上記従来技術のような二次的な問題も生じさせないことを、その解決すべき技術的課題とする。

【0011】

【着眼点】本件発明者は、ハロゲン酸の発生原因となる水分を除去する脱水剤を検討していた際に、脱水のみならず脱ハロゲン酸の機能をも有し、上記課題の解決に有効である、オルガノシラザン化合物を中心とする一定の有機ケイ素化合物群を発見するに至った。

【0012】

【課題を解決するための手段】

【0013】（第1発明の構成）上記課題を解決するための本願第1発明（請求項1に記載の発明）の構成は、水と反応してハロゲン酸を生じ得る支持電解質を含む非水電解液に、前記水及びハロゲン酸と反応してこれらを除去する、Si-N結合を有する有機ケイ素化合物を添加した電池用非水電解液である。

【0014】（第2発明の構成）本願第2発明（請求項1には記載していない）の構成は、少なくとも正／負極のいずれかの活物質としてリチウム又はその化合物を含み、かつ、第1発明に係る電池用非水電解液を用いる非水電解液電池である。

【0015】

【発明の作用・効果】第1発明において、非水電解液中に若干の水分が混入していたり、あるいはこの水分が支持電解質と反応してハロゲン酸が遊離していたりしても、これらの水分やハロゲン酸が前記の有機ケイ素化合物と反応することにより、除去される。なお、かかる作

用・効果は、第2発明においても同様である。

【0016】この有機ケイ素化合物と水、又はハロゲン酸との反応は非常に速やかに起こるため、特開平4-284372号に記載の発明のような反応速度の不足による不具合がなく、又、本発明においては特開平7-122297号公報に記載の発明のように二次的に他の有害物質を生ずると言う不具合もない。

【0017】以上のことから、本発明に係る電池用非水電解液においては、水と反応してハロゲン酸を生じ得る支持電解質を用いているにも関わらず、非水電解液に水が混入しても、電池構成材料の劣化や電池性能の劣化が阻止される。

【0018】

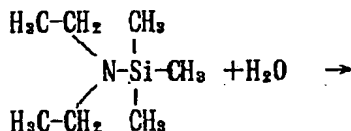
【発明の実施の形態】次に、第1発明、第2発明の実施の形態について説明する。

【0019】〔1. 本発明の対象〕原則として、水と反応してハロゲン酸を生じ得る支持電解質を含む電池用非水電解液及びこれを用いた非水電解液電池は、全て本発明の対象となり得る。現在のところ、非水電解液電池は、少なくとも正／負極のいずれかの電極活物質としてリチウム又はその化合物を用いる、いわゆる「リチウム電池」が殆どを占めている。

【0020】本発明の対象であるこのようなリチウム電池の2、3の例として、負極にリチウムを用いると共に正極には二酸化マンガ、フッ化亜鉛、酸化銅あるいは塩化チオニル等を用いるリチウム乾電池（一次電池）、負極にリチウム又はその合金を含むと共に正極には活性炭、二硫化チタンあるいは二硫化モリブデン等を用いるリチウム蓄電池（二次電池）、負極にリチウムイオンを吸蔵・放出できる炭素材料を用いると共に正極にリチウム遷移金属化合物を用いるリチウムイオン電池、等を挙げることができる。

【0021】なお、上記のようなリチウム電池でなくても、前記本発明の課題が生じ得る限りにおいて、本発明の対象たる電池用非水電解液、非水電解液電池である。

【0022】〔2. 支持電解質〕支持電解質とは、電池用非水電解液において、電解液の導電率を高めて電池の充電と放電を効率的に行うと言う目的で添加された物質を言う。良く知られた支持電解質に LiPF_6 や LiBF_4 があるが、本発明ではこれらに限定されず、他にも、例えば LiAsF_6 のように、水と僅かに反応してフッ化水素の *



【0028】

* ようなハロゲン酸を生じ得る支持電解質一般が含まれる。

【0023】〔3. 電池用非水電解液における有機溶媒〕支持電解質との特段のミスマッチングがない限りにおいて、有機溶媒の種類には限定がない。その2、3の例として、エチレンカーボネート（EC）、プロピレンカーボネート（PC）、ジエチルカーボネート（DEC）、ジメチルカーボネート、ジメトキシエタン、γブチロラクトン等や、これらの二種以上の混合溶媒を使用できる。

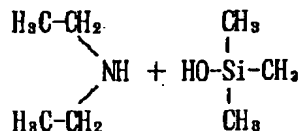
【0024】〔4. Si-N結合を有する有機ケイ素化合物〕本発明のSi-N結合を有する有機ケイ素化合物は、水やハロゲン酸との反応性に富み、そのSi-N結合が開裂することにより水やハロゲン酸を分解する能力を持つ。そして、反応後の分解生成物は電池性能に対して無害である。又、有機化合物であるから、非水電解液に対する親和性を有している。なお、上記の、「Si-N結合を有する有機ケイ素化合物」とは、分子中に単数又は複数のSi-N結合を有するものを含むのは当然として、その他に、分子中に例えばSi-N-Si結合と言う形でSi-N結合を有する有機ケイ素化合物をも包含する概念である。

【0025】Si-N結合を有する有機ケイ素化合物の代表的なものが、オルガノシラザン化合物や、オルガノジシラザン化合物である。これらに限らず、要するに有機化合物であり、かつSi-N結合を有するものである限り、その分子構造の如何を問わずに利用可能である。これらの化合物は単一種類のものを用いても、二種類以上のものを併用しても良い。

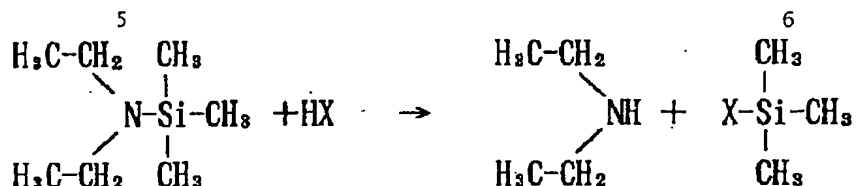
【0026】その内、オルガノシラザン化合物の2、3の例を挙げると、分子中に1つのSi-N結合を有する（N、N-ジエチルアミノ）トリメチルシラン、N、O-ビス（トリメチルシリル）アセトアミド等や、分子中に複数のSi-N結合を有するN、N'-ビス（トリメチルシリル）-1、4-ブタンジアミン等がある。例示として、（N、N-ジエチルアミノ）トリメチルシランと水との反応式を「化2」に、（N、N-ジエチルアミノ）トリメチルシランとハロゲン酸HXとの反応式を「化3」に示す。

【0027】

【化2】



【化3】

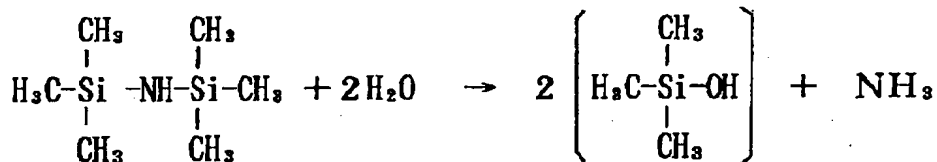


【0029】又、他のタイプの、オルガノジシラザン化合物やオルガノトリシラザン化合物等と呼ばれるオルガノシラザン化合物の例として、1, 1, 1, 3, 3, 3-ヘキサメチルジシラザンや、1, 1, 3, 3, 5, 5-ヘキサメチルシクロトリシラザンが挙げられる。例示として、1, 1, 1, 3, 3, 3-ヘキサメチルジシラザン*

* ザンと水との反応式を「化4」に、1, 1, 1, 3, 3, 3-ヘキサメチルジシラザンとハロゲン酸HXとの反応式を「化5」に示す。

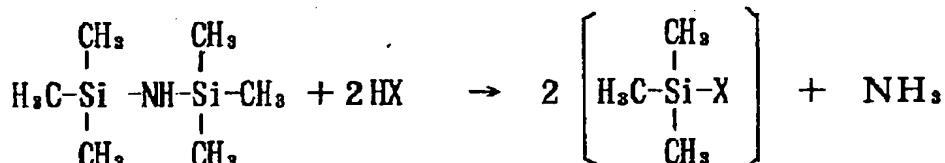
【0030】

【化4】



【0031】

※ ※ 【化5】



【0032】Si-N結合を有する有機ケイ素化合物の非水電解液に対する添加量については、非水電解液中の水分量が通常約1ミリモル/リットル以上であると言う理由から、これに対応して1ミリモル/リットル以上を添加することが好ましい。本発明の作用・効果の面からは、添加量の上限の限定はない。しかし、非水電解液の導電率を下げるという理由からは、0.5モル/リットルを超える添加は好ましくない。

【0033】以上のような本発明の有機ケイ素化合物を添加する方法には限定がなく、例えば電池組付け前に非水電解液に添加しても、電池組付け後の封缶前に電池容器内に直接添加しても良い。非水電解液に添加した有機ケイ素化合物の分散状態には別段の限定がない。

【0034】〔5. 非水電解液電池の正極〕正極の構成は、本発明の構成の主要部ではないから、本発明の構成の主要部と矛盾しない限りにおいて、何ら限定なく公知のあるいは任意の構成を採用することができる。

【0035】例えば非水電解液電池がリチウムイオン電池である場合には、正極の活物質としてLiCoO₂, LiNiO₂, LiMn₂O₄等の少なくとも一種と、導電助剤及びバインダとを混合溶剤にてペースト状にした合剤を、正極集電体であるアルミニウム箔の両面に塗布し、乾燥後、ロールプレス機にて圧縮成形するという手法を用いることもできる。

【0036】〔6. 非水電解液電池の負極〕負極の構成

は、本発明の構成の主要部ではないから、本発明の構成の主要部と矛盾しない限りにおいて、何ら限定なく公知のあるいは任意の構成を採用することができる。

【0037】例えば非水電解液電池がリチウムイオン電池である場合には、リチウムイオンを可逆的に吸蔵・放出できる易黒鉛化炭素、難黒鉛化炭素、黒鉛化材料等の任意の炭素材料を使用できる。そしてこれらの負極活物質の少なくとも一種とバインダとを混合溶剤にてペースト状にした合剤を、負極集電体である銅箔の両面に塗布し、乾燥後、ロールプレス機にて圧縮成形するという手法を用いることもできる。

【0038】上記の、非水電解液電池がリチウムイオン電池である場合における正極、負極のそれぞれの構成は、そのいずれか一方を、金属リチウムに置き換えることもできる。

【0039】〔7. 非水電解液電池の構成〕電池の全体的構成は、本発明の構成の主要部ではないから、本発明の構成の主要部と矛盾しない限りにおいて、何ら限定なく公知のあるいは任意の構成を採用することができる。

【0040】例えば電池形状については、円筒型、角型等に行うことができる。円筒型電池にする場合には、正極と負極とをセパレータを介して対向させ、円筒状に巻回し、これを電池缶に入れ電解液を注入するという一般的な方法を採用することもできる。

【0041】

【実施例】次に、第1発明及び第2発明の実施例について説明する。

【0042】【実施例1】三菱化学製の電解液（1mol/LのLiPF₆/EC+DEC(1:1)）50mLに対して、500ppmのイオン交換蒸留水と、その1.4倍モルの1, 1, 3, 3, 5, 5-ヘキサメチルシクロトリシラザン（チッソ製。以下、「HMTS」と言う）を加えて、サンプルびんに密封した。その試料を室温下に7日間放置した後、試料電解液中の酸量を0.1mol/LのNaOH水溶液（和光純薬工業製）で中和滴定法により定量した。

【0043】一方、比較のために、上記電解液に500ppmのイオン交換蒸留水を加えたがHMTSは添加しなかった例についても、同様にして定量を行った。

【0044】その結果、HMTSを添加しなかった例では加えられた水の2倍モルのフッ酸が検出されたが、HMTSは添加した例ではフッ酸が検出されなかった。

【0045】【実施例2】実施例1におけるHMTSに代えて、1, 1, 1, 3, 3, 3-ヘキサメチルジシラザン（チッソ製。以下、「HMD S」と言う）をHMTSと等モル量添加した点以外は全て実施例1と同じ条件で行った。

【0046】その結果、HMD Sを添加しなかった例では加えられた水の2倍モルのフッ酸が検出されたが、HMD Sを添加した例ではフッ酸が検出されなかった。

【0047】【実施例3】LiMn₂O₄（本荘ケミカル工業製）18.5重量部、アセチレンブラック（東海カーボン製）1.5重量部、ポリフッ化ビニリデン粉末（クレハ化学製）8重量部、N-メチルピロリドン（和光純薬工業製）72重量部を十分混合することにより、スラリーを得た。

【0048】このスラリーを、アブリケータを用いて厚さ20μmのアルミ箔（正極集電体）上に塗布し、乾燥プレスして、両面にLiMn₂O₄を塗布した厚さ160μmの正極材料を得た。

【0049】一方、黒鉛（大阪ガス製のMCMB）100重量部に対して、ポリフッ化ビニリデン粉末10重量部をN-メチルピロリドン100重量部に溶解した溶液100重量部を十分混合することにより、スラリーを得た。このスラリーを、アブリケータを用いて厚さ10μmの銅箔（負極集電体）上に塗布し、乾燥プレスして、両面に炭素材料を塗布した厚さ100μmの負極材料を得た。

【0050】そして、上記正極材料を直径15mmの円盤状に打ち抜いたものを正極に、上記負極材料を直径17mmの円盤状に打ち抜いたものを負極に、更にポリエチレンセパレータ（東燃化学製）を直径19.5mmの円盤状に打ち抜いたものをセパレータに用いて、正極と負極をセパレータを介して対向させたコイン型電池を作成した。

【0051】上記電池に、電解液として、三菱化学製の

1mol/LのLiPF₆/EC+DEC(1:1)にイオン交換蒸留水500ppmとその1.4倍モルのHMTS（チッソ製）を加えて60°Cで96時間加熱したものを、注入した。そして封缶して本例の試作電池とした。

【0052】これとは別に、HMTSを加えない点以外は上記と同一である比較用の試作電池も構成した。

【0053】上記本例及び比較用の試作電池について1mA/cm²の定電流で電池電圧が4.2Vになるまで充電し更に4.2Vの定電圧で充電を続け（充電時間の合計は6時間）、続いて0.5mA/cm²の定電流で電池電圧が3.0Vになるまでの放電を行う、と言う充・放電過程を1サイクルとして、これを繰り返すことによりサイクル劣化試験を行った。

【0054】その結果は図1に示す通りであり、HMTSの添加によって電池のサイクル特性が著しく改善されたことが分かる。

【0055】【実施例4】実施例3におけるHMTSに代えて、HMD S（チッソ製）をHMTSと等モル量添加した点以外は全て実施例3と同じ条件で電池を試作し、サイクル劣化試験を行った。

【0056】その結果は図2に示す通りであり、HMD Sの添加によって電池のサイクル特性が著しく改善されたことが分かる。

【0057】【実施例5】実施例3におけるHMTSに代えて、N, O-ビス（トリメチルシリル）アセトアミド（チッソ製。以下、「BSA」と言う）をHMTSと等モル量添加した点以外は全て実施例3と同じ条件で電池を試作し、サイクル劣化試験を行った。

【0058】その結果は図3に示す通りであり、BSAの添加によって電池のサイクル特性が著しく改善されたことが分かる。

【0059】【実施例6】実施例3におけるHMTSに代えて、（N, N-ジエチルアミノ）トリメチルシラン（チッソ製。以下、「DEATMS」と言う）をHMTSと等モル量添加した点以外は全て実施例3と同じ条件で電池を試作し、サイクル劣化試験を行った。

【0060】その結果は図4に示す通りであり、DEATMSの添加によって電池のサイクル特性が著しく改善されたことが分かる。

【図面の簡単な説明】

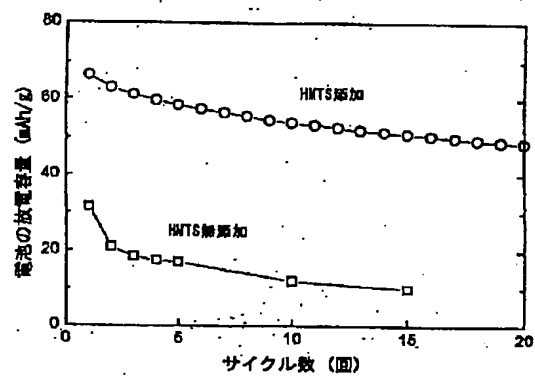
【図1】本発明例及び比較例の充・放電サイクル特性を示す図である。

【図2】本発明例及び比較例の充・放電サイクル特性を示す図である。

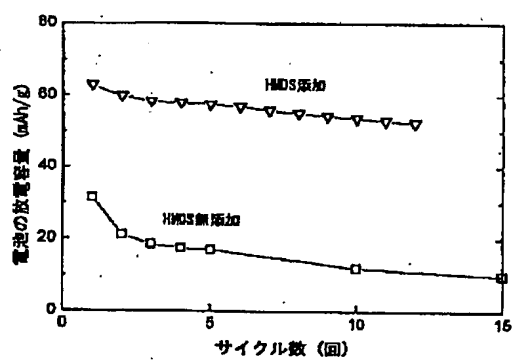
【図3】本発明例及び比較例の充・放電サイクル特性を示す図である。

【図4】本発明例及び比較例の充・放電サイクル特性を示す図である。

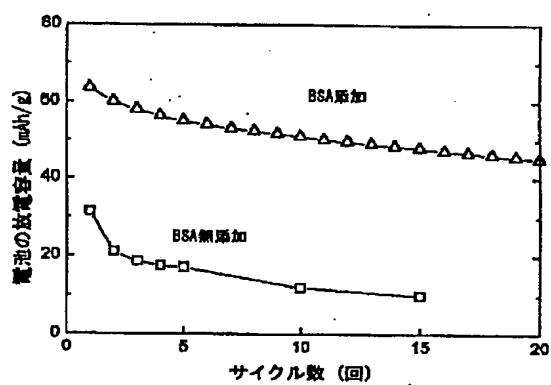
【図1】



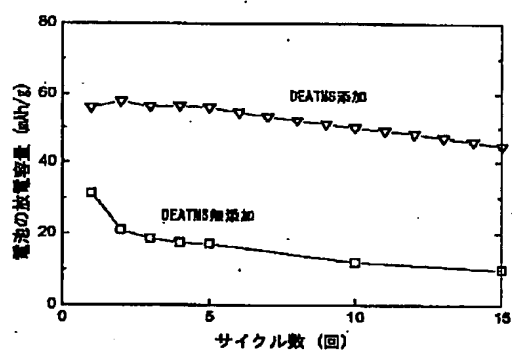
【図2】



【図3】



【図4】



JAPANESE

[JP,11-016602,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION
TECHNICAL PROBLEM MEANS EXAMPLE DESCRIPTION OF DRAWINGS DRAWINGS

[Translation done.]

* NOTICES *

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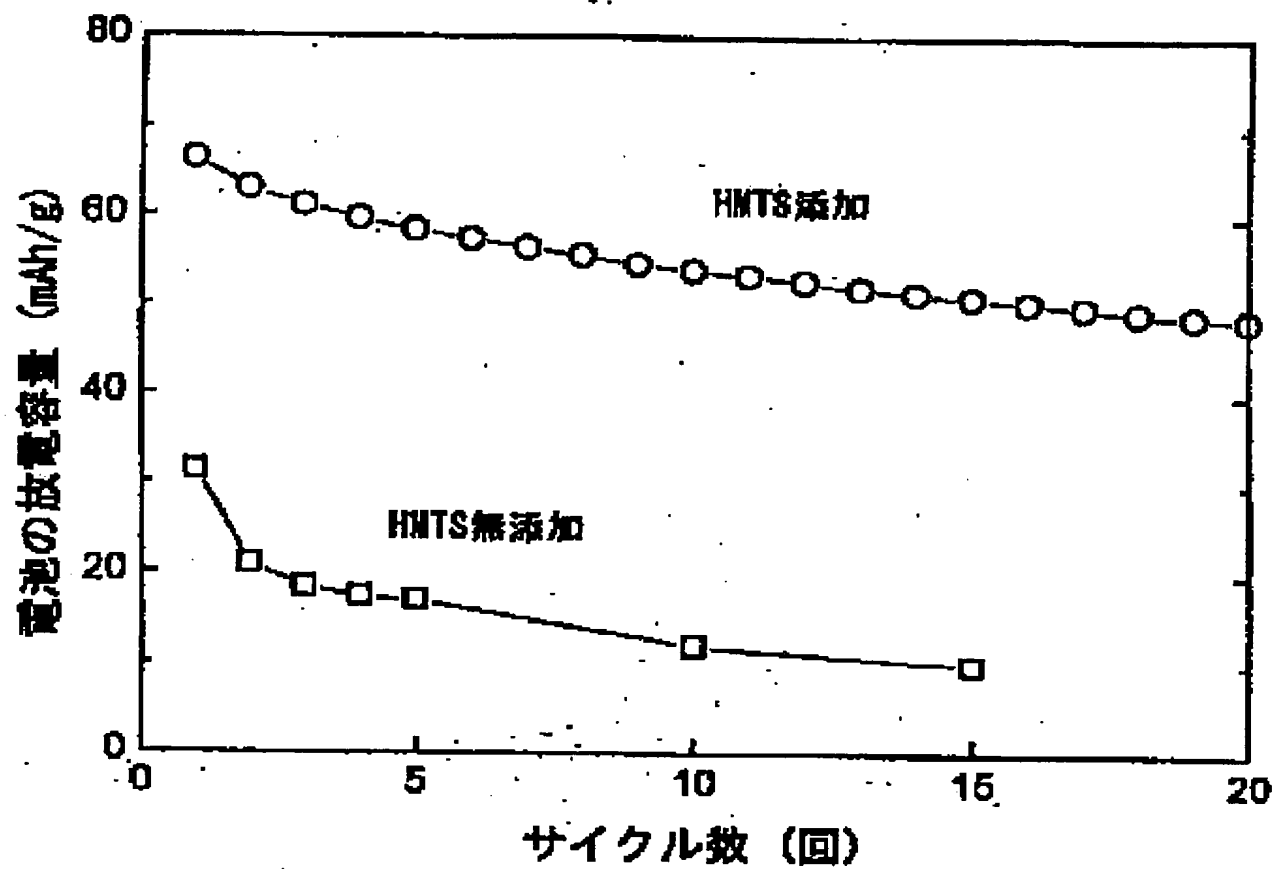
1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] Nonaqueous electrolyte for cells characterized by adding the organic silicon compound which has said water and halogen acid, and Si-N association which removes these in response to the nonaqueous electrolyte containing the supporting electrolyte which reacts with water and may produce halogen acid.

[Translation done.]



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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the nonaqueous electrolyte for cells which took the cure of originating in a small amount of moisture which may intervene unescapable about the nonaqueous electrolyte for cells in the lithium secondary battery using the nonaqueous electrolyte which used the fixed halogenated compound etc. as the supporting electrolyte in more detail etc., and halogen acid being generated.

[0002]

[Description of the Prior Art] A lithium or its compound is used for an electrode active material, and the nonaqueous electrolyte cell using the organic solvent which contains a supporting electrolyte as the electrolytic solution from that attracts attention in the usefulness as the rechargeable battery turned to the primary cell as for example, a small power source for electronic parts, and the dc-batteries of an electric vehicle, or a lithium ion battery.

[0003] in these nonaqueous electrolyte cells, it is a halogenated compound at the above-mentioned supporting electrolyte LiPF₆ etc. -- although used well, if some moisture is mixing unescapable into the electrolytic solution which must be non-water or the moisture produced by adsorption from other cell ingredients exists, a reaction as shown in the next "*** 1" will occur, and the halogen acid like hydrogen fluoride HF will be generated.

[0004]

[Formula 1]



[0005] Hydrogen fluoride has the problem referred to as degrading a cell component and degrading the cell engine performance further. Furthermore, it is known that the reaction of the above "*** 1" will be promoted by the pyrosphere. For this reason, for example, it especially sets to the rechargeable battery for dc-batteries of the electric vehicle with which stable actuation in the temperature region of -30-degreeC-60-degreeC is demanded, and a problem is a remarkable next door and LiPF₆. It is supposed that the nonaqueous electrolyte cell used as a supporting electrolyte is difficult to apply.

[0006] And in order to solve this problem, the following proposals are made conventionally. for example, it sets to invention of the nonaqueous electrolyte rechargeable battery indicated by JP,4-284372,A -- LiPF₆ the nonaqueous electrolyte used as a supporting electrolyte -- receiving -- aluminum 2O₃ MgO and BaO from -- by adding the oxide chosen, these oxides adsorb the hydrogen fluoride produced in the electrolytic solution, and it is supposed that it will remove out of the system of reaction.

[0007] Moreover, it is LiPF₆ if it sets to invention of the nonaqueous electrolyte cell indicated by JP,7-122297,A. It is supposed by adding an acid anhydride (for example, acetic anhydride) that these acid anhydrides catch the water in the electrolytic solution beforehand, and will control the reaction of the above "*** 1" to the nonaqueous electrolyte used as a supporting electrolyte.

[0008]

[Problem(s) to be Solved by the Invention] However, about invention given in said JP,4-284372,A, according to this artificer's supplementary examination, since removal of hydrogen fluoride advances very slowly depending on the oxide of the addition which can be actually permitted as a cell, it does not fulfill the generating rate of hydrogen fluoride. Therefore, there is a problem said for not coming to prevent degradation of the cell by hydrogen fluoride etc. effectively.

[0009] On the other hand, although the dehydration effectiveness by the acid anhydride is high about invention given in said JP,7-122297,A consequently, the acid resulting from an acid anhydride will be generated and, so to speak, it is only what permutes halogen acid by other acids. And as opposed to halogen acid, although an acetic acid etc. is weak acid relatively, there is no change in bringing about degradation of the electrolytic solution and a cell can ingredient too, and it has not become essential solution to it.

[0010] So, in this invention, in the nonaqueous electrolyte containing the supporting electrolyte which reacts with water and may produce halogen acid for cells, or the nonaqueous electrolyte cell using this, the evil by halogen acid is prevented effectively and let it be the technical technical problem which should be solved not to produce a secondary problem like the above-mentioned conventional technique moreover, either.

[0011]

[Focus] When this artificer is examining the dehydrating agent from which the moisture leading to [of halogen acid] generating is removed, he has not only dehydration but the function of a dehalogenation acid, and came to discover the fixed organic silicon compound group centering on the ORGANO silazane compound effective in solution of the above-mentioned technical problem.

[0012]

[Means for Solving the Problem]

[0013] (Configuration of the 1st invention) The configuration of the 1st invention (invention according to claim 1) of this application for solving the above-mentioned technical problem is nonaqueous electrolyte for cells which added the organic silicon compound which has Si-N association which removes these in response to the nonaqueous electrolyte containing the supporting electrolyte which reacts with water and may produce halogen acid with said water and halogen acid.

[0014] (Configuration of the 2nd invention) The configuration of the 2nd invention (it has not indicated to a claim) of this application is a nonaqueous electrolyte cell using the nonaqueous electrolyte for cells built over the 1st invention as an active material of either forward/negative electrode at least, including a lithium or its compound.

[0015]

[Function and Effect of the Invention] In the 1st invention, even if some moisture is mixing into nonaqueous electrolyte, or this moisture reacted with the supporting electrolyte and halogen acid has separated, when these moisture and halogen acid react with the aforementioned organic silicon compound, it is removed. In addition, this operation and effectiveness are the same also in the 2nd invention.

[0016] Since the reaction with this organic silicon compound, water, or halogen acid occurs very promptly, there is no fault by lack of a reaction rate like invention of a publication in JP,4-284372,A, and it does not have the fault referred to as producing other harmful matter secondarily like invention of a publication in JP,7-122297,A in this invention, either.

[0017] In spite of using the supporting electrolyte which reacts with water and may produce halogen acid from the above thing in the nonaqueous electrolyte for cells concerning this invention, even if water mixes in nonaqueous electrolyte, degradation of a cell component and degradation of the cell engine performance are prevented.

[0018]

[Embodiment of the Invention] Next, the gestalt of implementation of the 1st invention and the 2nd invention is explained.

[0019] [Object of 1. this invention] All the nonaqueous electrolyte cells using the nonaqueous electrolyte for cells and this containing the supporting electrolyte which reacts with water and may produce halogen acid in principle

can be set as the object of this invention. Now, the so-called "lithium cell" with which a lithium or its compound is used for a nonaqueous electrolyte cell at least as an electrode active material of either forward/negative electrode occupies most.

[0020] While using occlusion and the carbon material which can be emitted for the lithium battery (rechargeable battery) and negative electrode which use activated carbon, 2 titanium sulfides, or molybdenum disulfide for a positive electrode while a lithium or its alloy is included in the lithium dry cell (primary cell) and negative electrode which use a manganese dioxide, zinc fluoride, oxidation copper, or a thionyl chloride for a positive electrode as 2 of such a lithium cell that is the object of this invention, and an example of 3 while using a lithium for a negative electrode for a lithium ion, the lithium ion battery which uses a lithium transition-metals compound for a positive electrode can be mentioned.

[0021] In addition, even if it is not the above lithium cells, as long as the technical problem of said this invention may arise, they are the nonaqueous electrolyte for object slack cells of this invention, and a nonaqueous electrolyte cell.

[0022] [2. supporting electrolyte] A supporting electrolyte means the matter added in order to say that the conductivity of the electrolytic solution is raised and charge and discharge of a cell are performed efficiently in the nonaqueous electrolyte for cells. supporting electrolyte known well LiPF_6 LiBF_4 although it is, in this invention, it limits to these -- not having -- others -- for example, -- The general supporting electrolyte which reacts slightly with water and may produce halogen acid like hydrogen fluoride like LiAsF_6 is contained.

[0023] [Organic solvent in the nonaqueous electrolyte for 3. cells] As long as there is no mismatching special [with a supporting electrolyte], there is no limitation in the class of organic solvent. Ethylene carbonate (EC), propylene carbonate (PC), diethyl carbonate (DEC), dimethyl carbonate, dimethoxyethane, gamma-butyrolactone, etc. and two or more sorts of these mixed solvents can be used as the example of 2 and 3.

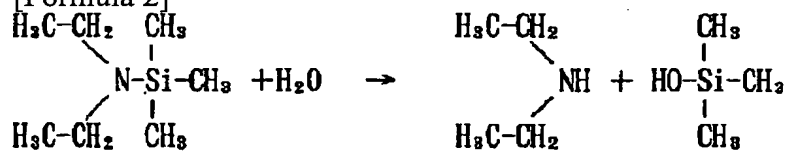
[0024] [Organic silicon compound which has 4.Si-N association] The organic silicon compound which has Si-N association of this invention is rich in reactivity with water or halogen acid, and when the Si-N association cleaves, it has the capacity which disassembles water and halogen acid. And the decomposition product after a reaction is harmless to the cell engine performance. Moreover, since it is an organic compound, it has the compatibility over nonaqueous electrolyte. In addition, the above-mentioned "organic silicon compound which has Si-N association" is a concept which also includes the organic silicon compound which has Si-N association in the form which it makes natural that what has an unit or two or more Si-N association is included in a molecule, in addition is called into a molecule for example, Si-N-Si association.

[0025] The typical things of an organic silicon compound which have Si-N association are the ORGANO silazane compound and an ORGANO disilazane compound. Not only these but in short, it is an organic compound, and as long as it has Si-N association, it is available, without asking how of the molecular structure. These compounds may use together two or more kinds of things, using the thing of a single class.

[0026] When 2 of the ORGANO silazane compound and the example of 3 are given, there are a trimethyl silane, an N.O-screw (trimethylsilyl) acetamide, etc. which have one Si-N association in a molecule (N and N-diethylamino), N [which has two or more Si-N association in a molecule], and N'-screw (trimethylsilyl)-1,4-butanediamine, etc. among them. As instantiation, the reaction formula of a trimethyl (N and N-diethylamino) silane and water is shown in "*** 2", and the reaction formula of a trimethyl (N and N-diethylamino) silane and halogen acid HX is shown in "*** 3."

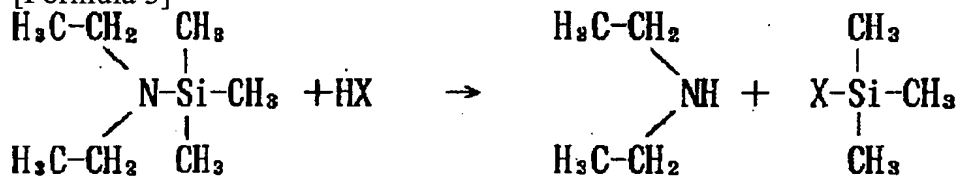
[0027]

[Formula 2]



[0028]

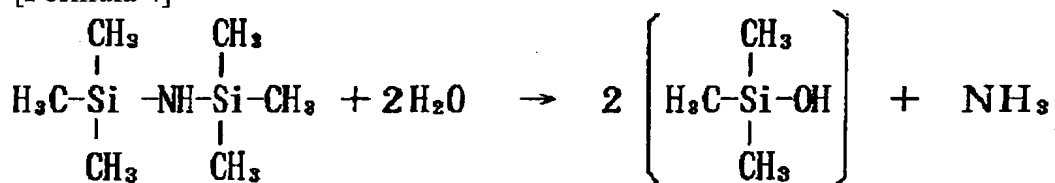
[Formula 3]



[0029] Moreover, 1, 1, 1, 3, 3, and 3-hexamethyldisilazane and 1, 1, 3, 3, 5, and 5-hexa methyl SHIKUROTORI silazane are mentioned as an example of the ORGANO silazane compound called an ORGANO disilazane compound, the ORGANO TORISHIRAZAN compound, etc. of other types. As instantiation, the reaction formula of 1, 1, 1, 3, 3, and 3-hexamethyldisilazane and water is shown in "*** 4", and the reaction formula of 1, 1, 1, 3, 3, and 3-hexamethyldisilazane and halogen acid HX is shown in "*** 5."

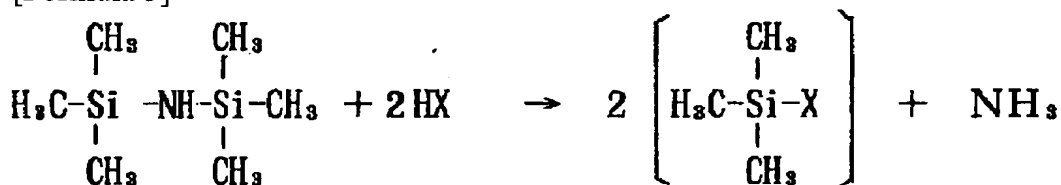
[0030]

[Formula 4]



[0031]

[Formula 5]



[0032] About the addition to the nonaqueous electrolyte of an organic silicon compound which has Si-N association, since it says that the moisture contents in nonaqueous electrolyte are usually more than about 1 millimol / liter, it is desirable to add more than 1 millimol / liter corresponding to this. There is no limitation of the upper limit of an addition from the field of the operation and effectiveness of this invention. However, since it says that the conductivity of nonaqueous electrolyte is lowered, the addition which exceeds 1. in 0.5 mols / is not desirable.

[0033] There is no limitation in the approach of adding the organic silicon compound of above this inventions, for example, it may add to nonaqueous electrolyte before cell attachment, or you may add directly in a cell container before the can sealing after cell attachment. Special limitation will be in the distributed condition of the organic silicon compound added to nonaqueous electrolyte.

[0034] [the positive electrode of 5. nonaqueous electrolyte cell] -- the configuration of a positive electrode is [that there is no limitation in any way] well-known unless it is contradictory to the principal part of the configuration of this invention, since it is not the principal part of the configuration of this invention -- it is -- it is -- the configuration of arbitration is employable.

[0035] the case where for example, a nonaqueous electrolyte cell is a lithium ion battery -- as the active material of a positive electrode -- LiCoO₂, LiNiO₂, and LiMn₂O₄ etc., at least, the mixture which made a kind, and an electric

conduction assistant and a binder the shape of a paste with the partially aromatic solvent can be applied to both sides of the aluminium foil which is a positive-electrode charge collector, and the technique referred to as pressing with a roll press machine can also be used after desiccation.

[0036] [the negative electrode of 6. nonaqueous electrolyte cell] -- the configuration of a negative electrode is [that there is no limitation in any way] well-known unless it is contradictory to the principal part of the configuration of this invention, since it is not the principal part of the configuration of this invention -- it is -- it is -- the configuration of arbitration is employable.

[0037] For example, when a nonaqueous electrolyte cell is a lithium ion battery, the carbon material of arbitration, such as occlusion, easily graphitized carbon which can be emitted, difficulty graphitized carbon, and a graphitization ingredient, can be reversibly used for a lithium ion. And at least, the mixture of these negative-electrode active materials which made a kind and the binder the shape of a paste with the partially aromatic solvent can be applied to both sides of the copper foil which is a negative-electrode charge collector, and the technique referred to as pressing with a roll press machine can also be used after desiccation.

[0038] Each configuration of a positive electrode in case the above-mentioned nonaqueous electrolyte cell is a lithium ion battery, and a negative electrode can also transpose the either to a metal lithium.

[0039] [the configuration of 7. nonaqueous electrolyte cell] -- the overall configuration of a cell is [that there is no limitation in any way] well-known unless it is contradictory to the principal part of the configuration of this invention, since it is not the principal part of the configuration of this invention -- it is -- it is -- the configuration of arbitration is employable.

[0040] For example, about a cell configuration, it can be made cylindrical, a square shape, etc. When making it a cylindrical cell, a positive electrode and a negative electrode can be made to be able to counter through a separator, and winding and the general approach referred to as putting this into a cell can and pouring in the electrolytic solution can also be adopted in the shape of a cylinder.

[0041]

[Example] Next, the example of the 1st invention and the 2nd invention is explained.

[0042] [an example 1] -- Mitsubishi Chemical electrolytic-solution (LiPF₆ / EC+DEC of 1 mol/L (1:1)) 50mL -- receiving -- 500 ppm ion-exchange distilled water and 1, 1, 3, 3 and 5 of the 1.4 time mol, and 5-hexa methyl SHIKUROTORI silazane (Chisso make.) the following and "HMTS" -- saying -- in addition, it sealed into the sample bottle. Acidity in the sample electrolytic solution after leaving the sample for seven days under a room temperature 0.1 mol/L The quantum was carried out by neutralization analysis in the NaOH water solution (product made from the Wako Pure Chem industry).

[0043] On the other hand, although 500 ppm ion-exchange distilled water was added to the above-mentioned electrolytic solution for the comparison, HMTS performed the quantum similarly about the example which was not added.

[0044] Consequently, although the fluoric acid of 2 double mol of the added water was detected in the example which did not add HMTS, fluoric acid was not detected in the example which added HMTS.

[0045] [Example 2] It replaces with HMTS in an example 1, and is 1, 1, 1, 3, 3, and 3-hexamethyldisilazane (Chisso make.). the following and "HMDS" -- saying -- it carried out on the same conditions as an example 1 except [all] the point which carried out equimolecular amount addition with HMTS.

[0046] Consequently, although the fluoric acid of 2 double mol of the added water was detected in the example which did not add HMDS, fluoric acid was not detected in the example which added HMDS.

[0047] [Example 3] The LiMn₂O₄ 18.5 (product made from Honjo Chemical industry) weight section, and acetylene black (Tokai Carbon make) The 1.5 weight sections and polyvinylidene fluoride powder (product made from KUREHA chemistry) The slurry was obtained by mixing enough 8 weight sections and the N-methyl pyrrolidone (product made from Wako Pure Chem industry) 72 weight section.

[0048] An applicator is used for this slurry and it is 20 micrometers in thickness. It applies on aluminum foil (positive-electrode charge collector), a desiccation press is carried out, and it is to both sides. LiMn₂O₄ Applied

thickness 160 micrometers The positive-electrode ingredient was obtained.

[0049] On the other hand, it is a graphite (Osaka Gas MCMB). It is N-methyl pyrrolidone about the polyvinylidene fluoride powder 10 weight section to the 100 weight sections. Solution which dissolved in the 100 weight sections. The slurry was obtained by mixing the 100 weight sections enough. An applicator is used for this slurry and it is 10 micrometers in thickness. Thickness which applied on copper foil (negative-electrode charge collector), carried out the desiccation press, and applied the carbon material to both sides 100 micrometers The negative-electrode ingredient was obtained.

[0050] And what pierced to the negative electrode what pierced to the positive electrode what pierced the above-mentioned positive-electrode ingredient to discoid with a diameter of 15mm, and pierced the above-mentioned negative-electrode ingredient to discoid with a diameter of 17mm, and pierced the polyethylene separator (Tonen Chemical make) to discoid with a diameter of 19.5mm further was used for the separator, and the coin mold cell which the positive electrode and the negative electrode were made to counter through a separator was created.

[0051] the above-mentioned cell -- as the electrolytic solution -- Mitsubishi Chemical 1 mol/L LiPF₆ / EC+DEC (1:1) -- 500 ppm of ion-exchange distilled water -- the -- What added HMTS (Chisso make) of a mol 1.4 times, and was heated by 60-degreeC for 96 hours was poured in. And can sealing was carried out and it considered as the prototype cell of this example.

[0052] Apart from this, the same prototype cell for a comparison as the above was also constituted except the point of not adding HMTS.

[0053] It is 1 mA/cm² about this above-mentioned example and the prototype cell for a comparison. Cell voltage by constant current It charges until it is set to 4.2V, and also charge is continued by the constant voltage of 4.2V (the sum total of the charging time is 6 hours), and it continues. 0.5 mA/cm² Cell voltage by constant current The cycle deterioration test was performed by repeating this by making into 1 cycle ** and the discharge process referred to as discharging until it is set to 3.0V.

[0054] The result is as being shown in drawing 1 , and it turns out that the cycle property of a cell has been remarkably improved by addition of HMTS.

[0055] [Example 4] It replaced with HMTS in an example 3, and except [all] the point which carried out equimolecular amount addition of the HMDS (Chisso make) with HMTS, the cell was made as an experiment on the same conditions as an example 3, and the cycle deterioration test was performed.

[0056] The result is as being shown in drawing 2 , and it turns out that the cycle property of a cell has been remarkably improved by addition of HMDS.

[0057] [Example 5] It replaces with HMTS in an example 3, and they are N and O-screw (trimethylsilyl) acetamide (Chisso make.). the following and "BSA" -- saying -- except [all] the point which carried out equimolecular amount addition with HMTS, the cell was made as an experiment on the same conditions as an example 3, and the cycle deterioration test was performed.

[0058] The result is as being shown in drawing 3 , and it turns out that the cycle property of a cell has been remarkably improved by addition of BSA.

[0059] [Example 6] It replaces with HMTS in an example 3, and is a trimethyl (N and N-diethylamino) silane (Chisso make.). the following and "DEATMS" -- saying -- except [all] the point which carried out equimolecular amount addition with HMTS, the cell was made as an experiment on the same conditions as an example 3, and the cycle deterioration test was performed.

[0060] The result is as being shown in drawing 4 , and it turns out that the cycle property of a cell has been remarkably improved by addition of DEATMS.

[Translation done.]

*** NOTICES ***

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is drawing showing ** and the discharge cycle property of the example of this invention, and the example of a comparison.

[Drawing 2] It is drawing showing ** and the discharge cycle property of the example of this invention, and the example of a comparison.

[Drawing 3] It is drawing showing ** and the discharge cycle property of the example of this invention, and the example of a comparison.

[Drawing 4] It is drawing showing ** and the discharge cycle property of the example of this invention, and the example of a comparison.

[Translation done.]

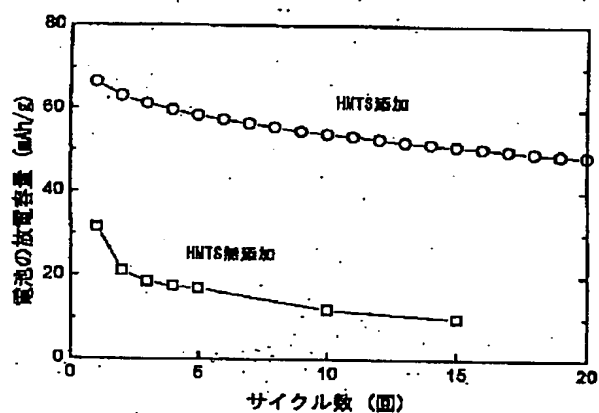
* NOTICES *

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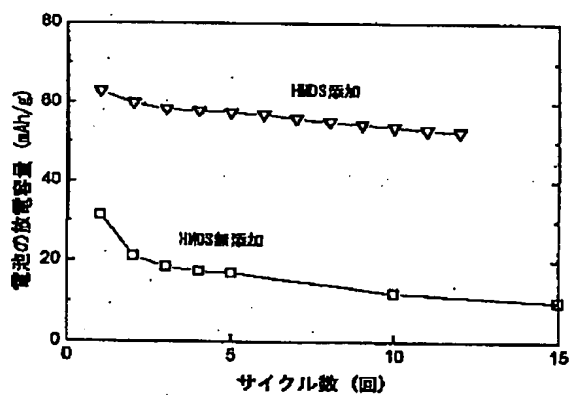
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DRAWINGS

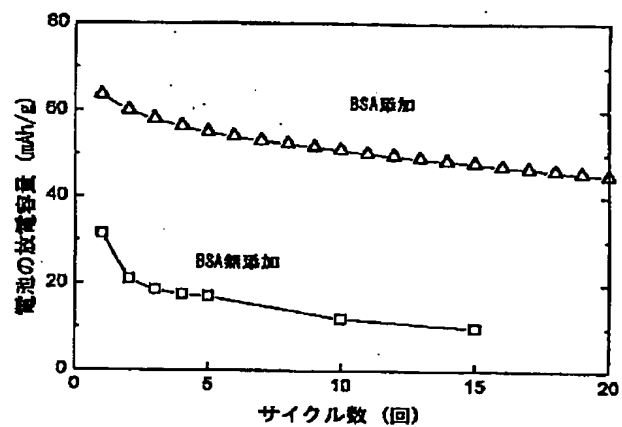
[Drawing 1]



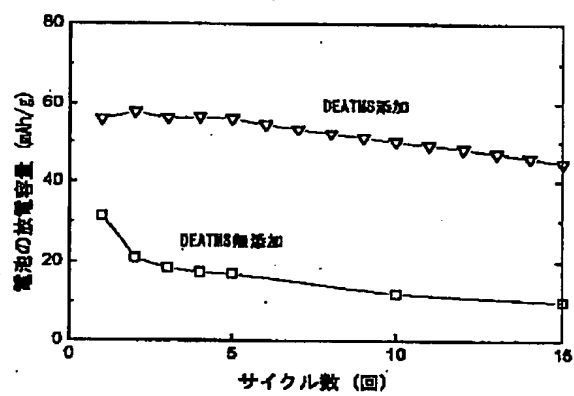
[Drawing 2]



[Drawing 3]



[Drawing 4]



[Translation done.]